

Optimization of Sintering Parameters of Submicron Cobalt Metal Powder Using Taguchi Method

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Abstract-The sintering studies of submicron cobalt powder have been presented in this paper. Cobalt powder prepared by thermal decomposition route of cobalt oxalate ($\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) has been characterized prior to sintering. In this investigation, the influence of various parameters affecting the sintering process has been analyzed and the optimum processing parameters for maximum sintered density have been determined by using Taguchi method. The parameters considered are the decomposition temperature, compaction pressure and sintering temperature. The effects of these input parameters on the response (percentage sintered density) have been critically analyzed using Taguchi method. It has been found that the sintering temperature is the most important process parameter affecting the sintered density. Sintered density near to theoretical density was obtained when the process parameters were set at their optimum values.

Keywords-Taguchi Method; Powder Metallurgy; Thermal Analysis; Sintering

I . INTRODUCTION

The applications of cobalt in the non nuclear field are wide spread, established and well documented in the literature. Sharma [1] enlighten the nuclear applications of cobalt including Gamma radiation source (^{60}Co) for a variety of industrial and medical applications, Self Powered Neutron Detectors (SPNDs) for in-core power measurements, flux mapping, fuel management etc. An efficient flow sheet for recovering cobalt from spent ammonia Cracker catalyst, as a secondary source has previously been established employing hydrometallurgical route in the author's lab [2-5]. In this process, the spent catalyst is finally converted to cobalt oxalate di-hydrate, which is thermally decomposed under reducing conditions to produce submicron sized pure cobalt powder. Once a homogeneous alloy powder is prepared, the next important task is to convert it into desired shapes with appropriate mechanical and physical properties. For using cobalt as a radiation source (^{60}Co), the shapes have to qualify for sintered density apart from dimension and chemical purity. Sintering of the powder therefore becomes of utmost importance during shaping. Many factors like characteristics of powder, compaction pressure, sintering time, sintering temperature, and sintering atmosphere affect the overall sintering process. The main purpose of this paper is to establish the significant factors that influence the process of sintering for cobalt powder. This can be determined through a series of experiments. For k number of parameters at n different levels the total number of experiments to be done is nk . However, such experiments are expensive and time-consuming. Design of experiment (DOE) techniques like the Taguchi method can optimize process parameters with minimum number of experiments. Taguchi method [6,7] is especially suitable for industrial use, but it has been also used for scientific research. Numerous researches have carried out experiments for determining optimum process parameters of

various manufacturing processes using Taguchi method. Taguchi method has been applied successfully by Dasgupta et al. [8] for controlling purity of carbon nano tubes, Davidson et al. [9] for flow forming of AA6061 alloy, Chua et al. [10] for microstructure and properties of sintered PZT, Alauddin et al. [11] for prediction of tool life in end milling. Berginc et al. [12] and Ahmed et al. [13] have used Taguchi method for optimization of sintering parameters for injection mouldings and Ti foams respectively.

In this study, three independent process parameters, namely decomposition temperature, compaction pressure and sintering temperature have been chosen as the controlling parameters for sintering of cobalt powder for implementing DOE. Sintering time is also an important process parameter for sintering. As sintering time is function of temperature, the first optimum sintering temperature has been determined keeping sintering time constant. Once the optimum sintering temperature is determined, the effect of sintering time has been studied by dilatometer. All the three parameters chosen varied in three different levels. So, this is a three factors three levels system and Taguchi method allows us to carry out only nine experiments to establish the most significant factor that influences the process of sintering.

Besides the optimization of processing parameters, the influence of thermal decomposition temperature of cobalt oxalate on cobalt powder characteristics like size, shape, purity, tap density and morphology has been studied. The effect of compacting pressure, sintering temperature and time on degree of sintering of green compacts made by cobalt powder of different characteristics has been studied to attain targeted density of >95 % of theoretical.

II . experimental details

A. Preparation and Characterization of Cobalt Powder

Cobalt oxalate di-hydrate $\text{Co}(\text{OOC})_2 \cdot 2\text{H}_2\text{O}$, produced by the method reported earlier by Sadanandam et al. [4] was used for obtaining cobalt metal powder. The chemical composition of cobalt oxalate was 0.052 % Ni, 0.005% Al, 0.016% Fe and 0.005% Cu, and balance Co with average particle size of 33 μm . The reaction sequences involved in the preparation of cobalt by thermal decomposition of cobalt oxalate were studied by thermogravimetric technique (TG), using Setaram Thermoanalyser (Model SETSYS 2408 model). The cobalt oxalate powder sample was heated at 5°C min^{-1} to determine onset temperatures and completion of thermal decomposition. Cobalt powder was characterized with respect to particle size, size distribution, tap density and phases. Particle size analysis of the powder samples were carried out in a laser particle analyzer. Particle size and powder morphology were examined by scanning electron microscope (Model

MV2300CT/100, Camscan, UK) and crystallite size was measured by XRD line broadening. A powder X-Ray Diffractometer with graphite monochromator and MoK α radiations was used for the analysis of phases present and its distribution. The powder was scanned in 20 range of 10 to 40 degree with scanning rate of 2 degree per minute. Tap densities of the powders were measured in order to find out the flow ability of the powders. Tap Density was determined using ASTM B527 - 06 standard test methods.

Cobalt powder samples prepared by thermal decomposition of cobalt oxalate at different temperatures were used in sintering studies. Powder compacts compacted at 180 MPa, 220 MPa, 250 MPa and 300 MPa were subjected to sintering at different temperatures from 973K (700°C) to 1573K (1300°C). The dual push type horizontal dilatometer was used for sintering study. The heating was done at 10 K per minute up to 1573K (1300°C) to monitor the shrinkage profile during sintering. Green densities were measured using the geometrical dimensions. Density after sintering was measured by Archimedes Principle as well as geometrical method. The microstructures of the sintered samples at various stage of sintering were observed under optical microscope and scanning electron microscope (SEM).

B. Experimental Setup for Decomposition of Cobalt Oxalate

A specially designed vertically mounted, cylindrical silica reactor was used for decomposition of cobalt oxalate. The schematic of the decomposition reactor is shown in Fig.1.

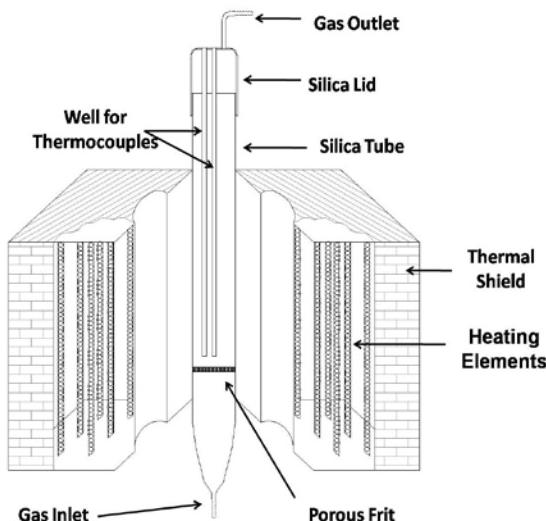


Fig. 1 Schematic diagram of decomposition reactor

The reactor was placed in a resistance heating furnace. The reactor has been designed for a reaction zone of 200mm. The dimension of the reactor is 100mm diameter and 1000mm height. It consists of a very fine silica frit, which acts as gas inlet for reaction zone. The experiments were conducted at temperatures of 723K (450°C), 823K (550°C) and 873 K (600°C) keeping soaking duration constant at 30 minutes in flowing Argon-hydrogen atmosphere (80:20 by volume) with a flow rate of 20 ml/ min. Prior to discharge of the cobalt powder from the reactor it was subjected to a "conditioning" treatment. In the conditioning treatment, controlled surface oxidation was promoted by passing carbon di-oxide gas for a short duration to prevent any possibility of instant ignition of

freshly generated powder. Conditioning treatment is essential for Co powder because it is pyrophoric in nature.

C. Experimental Design Using Taguchi Approach

Three parameters and the three levels for each parameter have been chosen which are tabulated in Table I . Taguchi's L9 orthogonal array for conducting experiments has been shown in Table II .

TABLE I FACTORS AND FACTOR LEVEL SELECTED IN THE EXPERIMENT

Parameter	Level 1	Level 2	Level 3
Decomposition Temperature (D _T)	450°C	550°C	600°C
Sintering Temperature (S _T)	1100 °C	1200 °C	1300 °C
Compaction pressure (C _P)	200 MPa	250 MPa	300 MPa

TABLE II TAGUCHI'S L9 ORTHOGONAL ARRAY FOR THE EXPERIMENT

Exp. No.	D _T (°C)	S _T (°C)	C _P (MPa)	Sintered Density	S/N (dB)
1	450	1100	200	7.2	17.15
2	450	1200	250	7.8	17.84
3	450	1300	300	8.2	18.27
4	550	1100	250	7.5	17.50
5	550	1200	300	7.7	17.72
6	550	1300	200	8.4	18.48
7	600	1100	300	7.4	17.38
8	600	1200	200	7.5	17.50
9	600	1300	250	8.4	18.48

Since in this case there is a feasibility to perform multiple runs for each of the experimental parameters provided by the design matrix, the Taguchi analysis was performed by using S/N ratio analysis. Barker et al. [14] reported that the S/N ratio is a concurrent quality metric linked to the loss function. By maximizing the S/N ratio, the loss associated can be minimized. The S/N ratio determines the most robust set of operating conditions from variation within the results. In the present work, three runs were performed for each of the nine experiments.

III. RESULTS

A. Thermal Decomposition of Cobalt Oxalate in Thermobalance

The result of TG study conducted under hydrogen atmosphere has been shown in Fig.2. It clearly reveals occurrence of two thermal events. First, a weight loss of approx. 19% occurs at around 423K (150 °C), suggesting

dehydration of cobalt oxalate di-hydrate (theoretically 19.68% for loss of 2 moles of water).

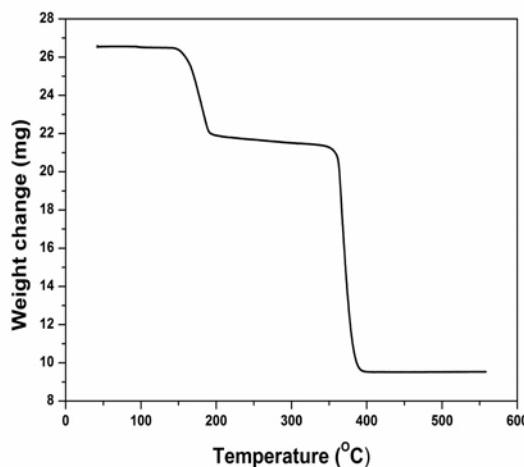


Fig. 2 Plot of decomposition characteristic of cobalt oxalate obtained by TG

The second endothermic event occurs at 643K (370°C) and is accompanied by a weight loss of 47%, which brings the total loss to 66% of the original weight. Such weight loss is equivalent to the value calculated for $C_2O_4Co \cdot 2H_2O$ to Co transformation. The cobalt metal powder prepared at 643K (370°C) exhibited highly pyrophoric nature. An increase in the particle size of cobalt powder, which could be accomplished by conducting decomposition reaction at a suitable temperature higher than 643K(370°C) could overcome the pyrophoric nature. Sharma et al. [15] studied the effect of temperature on yield (percentage conversion) and purity of different Cobalt compounds (including cobalt oxalate) to cobalt. According to their findings, maximum achievable conversion from cobalt oxalate to cobalt metal takes place within half an hour beyond 773K (500°C), matching with present results.

B. Characterization Studies

Fig.3 and Fig.4 show the SEM images of cobalt oxalate used in the entire experiment campaign and cobalt metal powder prepared at 823 K (550°C) respectively. The SEM image of cobalt powder reveals an agglomerated morphology. Tikkannen et al. [16] also reported similar agglomerated morphology of cobalt powder after decomposition from cobalt oxalate.

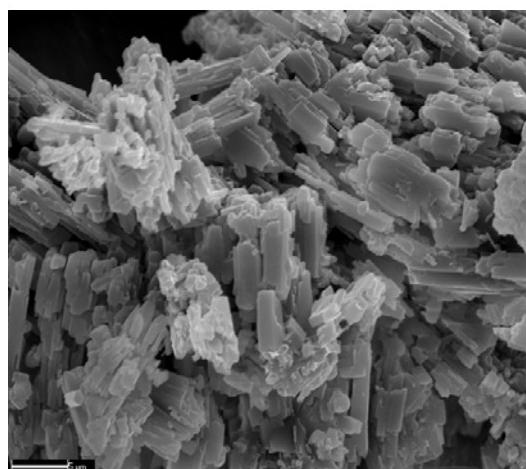


Fig. 3 SEM image of cobalt oxalate used in experiment

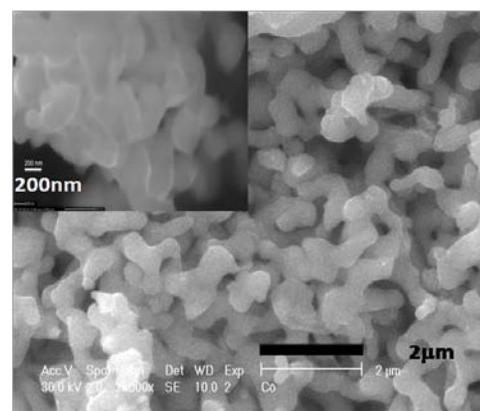


Fig. 4 SEM microphotographs of cobalt powder formed 823K (550°C). Inset shows the magnified image at same location

The morphologies of cobalt powders prepared at different temperatures do not differ significantly except the agglomerate size. The average agglomerate size measured from SEM images was $23 (\pm 3) \mu m$, close to the values evaluated through laser particle size analyzer i.e. 12, 18 and $23 \mu m$ for powders prepared at 773 (500°C), 823 (550°C) and 873 K (600°C), respectively. It is to be noted that unavailability of suitable dispersant for the particle size analysis resulted in average agglomerate size determination instead of individual particle size. However, the average crystallite size, clearly visible in the inset of Fig.3 is around 200 nm and reveals the sub-micron nature of the metal powder. The particle size distribution of cobalt powder prepared at various temperatures is graphically presented in Fig. 5.

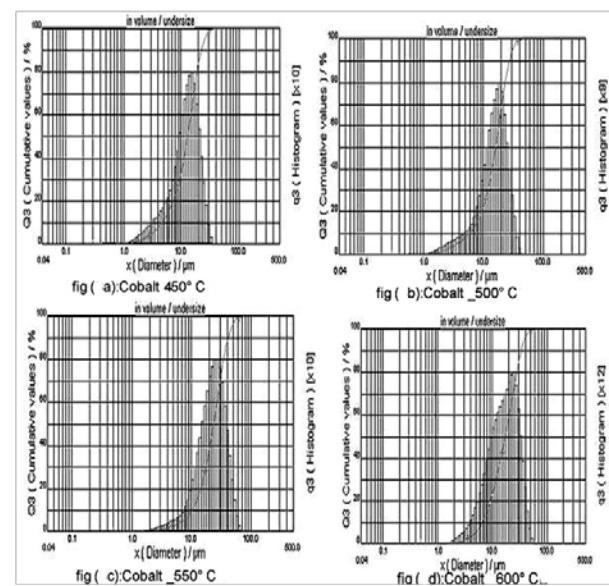


Fig. 5 Particle size distribution of cobalt powder decomposed at different temperature

The size distributions pattern was similar in all the cases and the curves tend to shift right with increasing decomposition temperature. It was found that the average particle size increased from $12.81 \mu m$ for powder thermally decomposed at 723K (450°C) to $23.67 \mu m$ for powder thermally decomposed at 873K (600°C). Tap densities were also increased with the decomposition temperature. This is because at higher decomposition temperature both the particle size and the agglomerate size are coarser.

C. Phase Analysis

The XRD pattern of cobalt powder decomposed at 723 K (450°C), 823 K (550°C) and 873 K (600°C) is shown in Fig. 6 which shows that Co-powder is mixture of FCC and HCP having 37%, 12% and 10% HCP phase respectively.

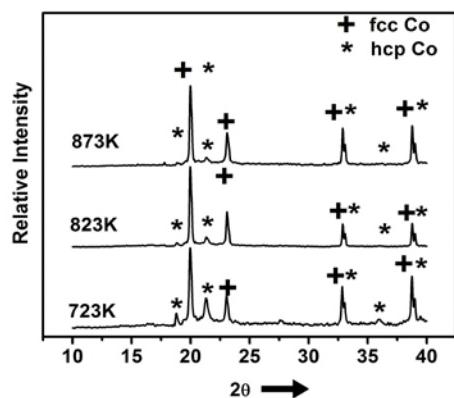


Fig. 6 XRD pattern of cobalt powder decomposed at 723 K (450°C), 823 K (550°C) and 873 K (600°C)

Kitakami et al. [17] showed that, there is a complete change in crystal structure of the cobalt powder from HCP to FCC on heating above 693 K (420°C) but it never complete during cooling cycle. Because of the incomplete transformation the thermally decomposed powder was consists of two phases having different proportions of retained FCC phase. The extent of retained FCC or the phase distribution is important in assessing the compressibility of powder. During compaction, compression of powder generally takes place by rearrangements of the powder particles, elastic distortion, and shear deformation causing mechanical flow and finally by breaking. Since FCC is more ductile phase, higher content of FCC would lead to higher compressibility than powder having lower content FCC phase. Thus higher the FCC content of the powder, higher would be the compressibility resulting higher green density.

D. Calculation and Analysis of Results of Taguchi Optimization Experiments

Taguchi method is widely used for identification of the optimal combination of factors for the desired results. Traditional experimentation involves one parameter at a time, where one variable is changed keeping rest of the variables fixed. Using conventional method, it is not possible to find any interactions between the parameters. It is also not possible to study all the parameters involved in the process and to determine their main effects (i.e., the individual effects) in a single experiment. Taguchi technique has the ability to take care of these drawbacks.

In the analysis, S/N ratio is the statistical quantity representing the power of a response signal divided by the power of the variation in the signal to noise. Since maximization of the properties is the goal of this study, the signal to noise ratios for the "larger-the-better" can be adopted, using the following formula:

$$S/N = -10 \log * \left| \frac{1/y_1^2 + 1/y_2^2 + \dots + 1/y_n^2}{n} \right| \quad (1)$$

where y_i is the measured property and n corresponds to the number of times experiments have been conducted. In the

present study, the interaction between the factors is neglected. The properties obtained from each experiment have been analyzed statistically. The effect of a parameter level on the S/N ratio, i.e., the deviation it causes from the overall mean signal, is obtained by analysis of mean (ANOM). The relative effect of process parameters can be obtained from analysis of variance (ANOVA) of S/N ratios. Computation of ANOM and ANOVA are done by using following relations.

$$\text{Sum of square (SoS)} = \sum_{i=1}^{i=j} N_i (m_i - \langle m_i \rangle)^2 \quad (2)$$

where m_i represents the contribution of each parameter level to S/N ratio, $\langle m_i \rangle$ is the average of m_i 's for a given parameter and the coefficient and N_i represents the number of times the experiment is conducted with the same factor level in the entire experimental region. SoS is obtained using ANOVA. Relative importance of various experimental parameters can be derived from the equation-(3).

$$\text{Factor effect} = \frac{SoS}{\{DoF \times \sum (SoS / DoF)\}} \quad (3)$$

where DoF (degrees of freedom) = (number of parameter level – 1)

The results of the experiments as per the L-9 array and the corresponding S/N ratios are given in Table II. The effects of each parameter on the final sintered density have been calculated by Eqs. (1)–(3) is shown in Table III. Fig. 7 shows the effects and their variation between levels of the parameters on the final sintered density graphically.

TABLE III EFFECT OF DIFFERENT PARAMETERS ON SINTERED DENSITY

Factor	Level	Sintered Density	m_i	$\langle m_i \rangle$	SoS	% Effect
D_T	450	7.73	17.75	17.81	0.0126	1.90%
	550	7.86	17.90			
	600	7.76	17.78			
S_T	1100	7.37	17.34	17.81	0.6	90.75%
	1200	7.67	17.68			
	1300	8.33	18.41			
C_P	200	7.70	17.71	17.84	0.0485	7.33%
	250	7.90	18.01			
	300	7.77	17.79			

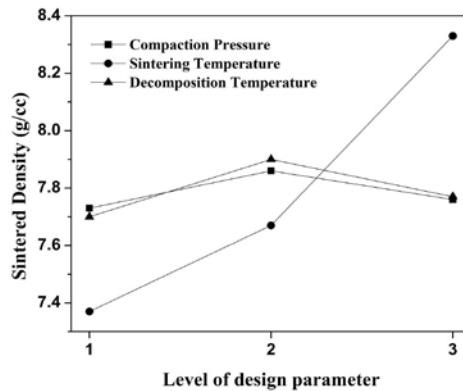


Fig. 7 The graphical representation the main effects and their variation between levels of the parameters on the final sintered density

The relative slope of the linear graphs indicates significance of the different parameters. It is observed that the sintering temperature (S_T) has a maximum effect (~90%) and the decomposition temperature has a minimum effect (~2%) on the final sintered density. Paul et al. have also found that the temperature was the most significant factor because of the higher activation energy (373 kJ/mol) associated with the cobalt system.

IV. DISCUSSION

The effect of compaction pressure on the green density of cobalt compact has been graphically depicted in Fig. 8(a). The rate of change of green density with compaction pressure differs in each case but becomes noticeable in the range of 250 to 300 MPa. Also, since the powder decomposed at 873 K (600°C) constitute maximum percentage of FCC phase, it shows highest compressibility. The compacts were subsequently sintered at 1573 K (1300°C) under H_2 atmosphere for one hour and the results are presented as the effect of compaction pressure on sintered density is presented in Fig. 8 (b)

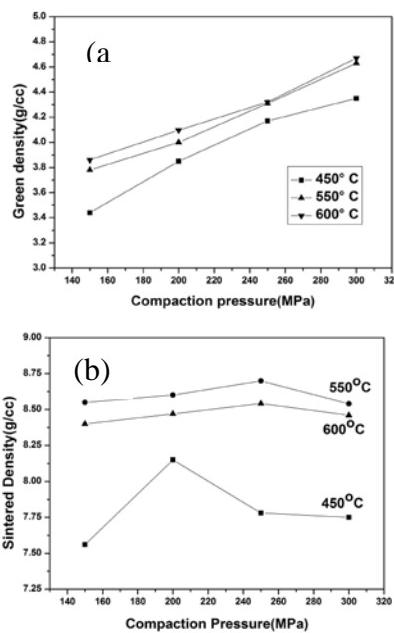


Fig. 8 (a) Plot of compaction pressure versus green density; (b) Plot of compaction pressure versus sintered density

In general, as the applied compaction pressure increases, the green density increases and so the sintered density. But the present study has revealed that after a particular compaction pressure sintered density decreases (Fig. 8 (b)). The maximum sintered density was attained at intermediate compaction pressure for all the powders. Marinkovic et al. [18] reported that the application of higher pressure can lead to cold sintering amongst the particles. Due to the cold sintering amongst powders, they now appear several times larger than the actual particle size and therefore reduce the driving force for sintering. Panigrahi et al. [19] also reported similar observation that application of higher pressure results in strong agglomerates amongst particles, which leads to decrease in sintering rate and total shrinkage because the inter-agglomerate pores remain un-sintered even at later stages of sintering. On the other hand, cobalt powder of much lower average particle size (decomposed at lower temperature)

could not attain the highest sintered density. Because of its higher surface area results in higher probability of oxidation could be cited as one of the possible reasons. Due to the more surface oxidation, thin oxide film covers the particles which reduce the diffusivity and in turn sinter ability. The oxide layer on the particles obstructs the formation of metallic bond between them during initial stage of sintering. Paul et al. [20, 21] have reported that hydrogen however can diffuse into the pores interstitially and facilitates densification via reaction with the oxides to some extent. Thus it can be inferred that the sinter ability is best for powder prepared at intermediate decomposition temperature 823K (550°C) and compacted at intermediate pressure (250 MPa). Fig. 9 shows the SEM image of sintered cobalt which has been sintered at 1300°C showing the equiaxed grains of size 3-4 μm with minimum pores (<5%).

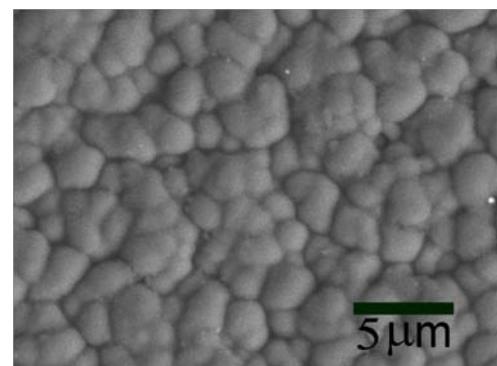


Fig. 9 the SEM image of cobalt sintered at 1573 K (1300°C)

These observations clearly point towards the fact that, the particle size, size distribution, morphology, and the phases present in cobalt powder play decisive role in the attainment of final sintered density. The effect of different factors affecting directly or indirectly to process of sintering have been shown schematically in Fig. 10 for the present system.

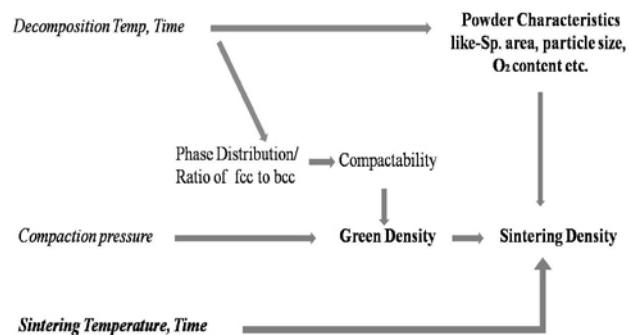


Fig. 10 Flow sheet showing the parameters which affect the process of sintering directly (in bold) and indirectly. The operating parameters are shown in italic

Initially some expansion is seen due to the thermal expansion and expansion of gases entrapped in green pellets. The highest shrinkage rate was observed at 1073K (800°C). It also indicates that on completion of soaking duration of an hour, shrinkage rate practically becomes zero. Thus the holding time of 1 hour at 1573 K (1300°C) is sufficient to achieve the targeted density. It can also be seen in Fig. 11 that the shrinkage increases from 13% at 1273K (1000°C) to 17% at 1573K (1300°C), where the density exceeded the targeted level and attained 95.7% (sintered density=8.5g/cc,) of the theoretical value (density of cobalt= 8.9 g/cc).

Based on the above findings, Co powder decomposed at 823K (550°C) and compacted at 250 MPa was taken up for finding an optimum temperature of sintering by dilatometric study. From the dilatometric curve shown in the Fig. 11, it can be inferred that significant shrinkage started at around 883 K (610°C), and continued up to 1573 K (1300°C).

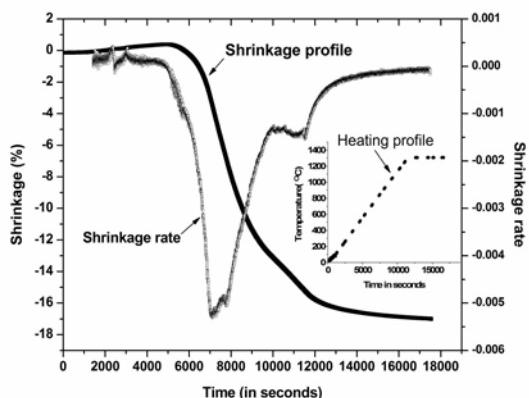


Fig. 11 Plot of shrinkage profile and shrinkage rate with sintering schedule

V. CONFIRMATION TEST

For the validation of the Taguchi method, confirmation test is required. Fig. 7 reveals that for maximum sintered density, decomposition temperature (D_T) should be at Level 2, compaction pressure should be at Level 2 and sintering temperature should be at Level 3. Confirmation run was performed to validate the model generated using input parameter values as: $D_T = 823$ K (550 °C), $C_p = 250$ MPa and $S_T = 1573$ K (1300 °C). The sintered density using these input parameters was found to be >8.6g/cc validating the Taguchi approach. Specific cobalt shapes (Co slugs, $\Phi 6\text{mm} \times L25\text{mm}$ and pellets, $\Phi 1\text{mm} \times L1\text{mm}$) used as a radiation source have been fabricated using powder metallurgy route using the suitable levels of process parameters determined by Taguchi method. Fig. 12 shows some of the shapes produced following the above mentioned optimum parameters.

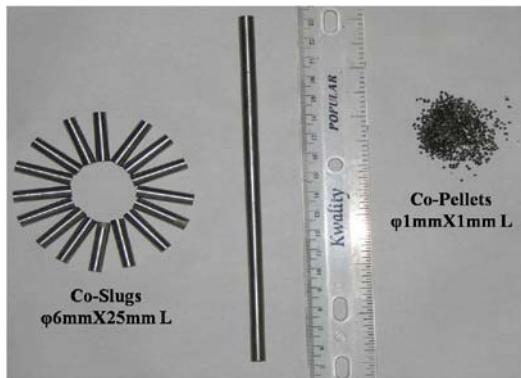


Fig. 12 Some of the shapes produced following the optimum parameters

VI. CONCLUSIONS

The Taguchi method was effectively used to determine the effects of different parameters on sintered density of cobalt. The optimum conditions for preparation of cobalt pellets of highest sintered density could be summarized as: thermal decomposition temperature 823 K (550°C), time 0.5 h, Compaction pressure -250 MPa, temperature of sintering 1573

K (1300°C), period of 1 h, maintaining reducing atmosphere. Besides the optimization of process parameters, the influence of temperature and time of thermal decomposition of cobalt oxalate, on cobalt powder characteristics like size, shape, purity, and morphology has been studied. Following the established optimum parameters different shapes for radioactive source with 97% of theoretical density could be fabricated.

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